High Energy Density Li-ion Cells for EV's Based on Novel, High Voltage Cathode Material Systems

Keith D. Kepler
Farasis Energy, Inc.

6-18-2014

This presentation does not contain any proprietary, confidential or otherwise restricted information

Project ID: # ES213

Overview

Timeline

- Start Date: October, 2013
- End Date: October, 2015
- Percent Complete – 20%

Barriers

- Insufficient energy density of Li-ion battery systems for PHEV and EV applications.
- Insufficient cycle and calendar life of Li-ion battery systems.
- Accelerated energy loss at elevated voltages for Li-ion technology.

Budget

- Total Project Funding: $3,480,000
  - -DOE Share: $2,160,000
  - -FFRDC: $600,000
  - -Contractor Share: $720,000
- 2013 Funding: *~$300,000*
- *Funding for 2014: ~$1,400,000*

Partners

- Argonne National Laboratory:
  - ➢ *Advanced Cathode Materials Development*
- Lawrence Berkeley National Laboratory:
  - ➢ *Advanced Cathode Materials Development*
- Dupont:
  - ➢ *High Voltage Electrolyte, Separator Development*
- Nanosys/OneD Material, LLC:
  - ➢ *High Capacity Anode Materials Development*

Relevance

- New cathode and anode electrode materials and Li-ion cell components are required to enable major advances in the energy density of battery systems for transportation technologies.
- The layered and layered-layered "NMC" class of cathode materials paired against a silicon based anode offer the greatest potential to meet the PHEV and EV performance goals.
- Utilization of the inherent capacity in these systems can be greatly increased if higher voltage operation can be enabled.
- There are multiple interacting failure mechanisms at the materials and cell level that are barriers to achieving the system level battery performance goals.
- A focus on cell level development utilizing advanced materials and components is critical to achieving major breakthroughs in battery performance.

Relevance - Project Objectives

Project Goal:

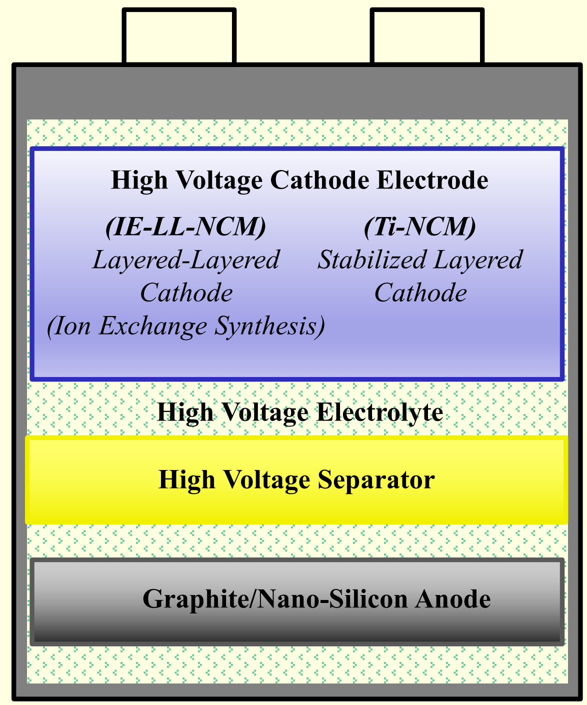
The goal of this project is to develop and demonstrate new high energy, high voltage capable Li-ion materials and cell components to enable high energy, high power Li-ion cells that have the potential to meet the performance goals of PHEV40 and EV light-duty vehicles.

Performance Objective:

The objective is to demonstrate a PHEV40 cell with an energy density of 250 Wh/kg and an EV light duty cell with an energy density 350 Wh/kg that can meet the cycle life goals for those applications.

Cell Level Goals:

Energy Storage Requirements			
Characteristics	**Unit**	**PHEV40**	**EV**
Specific Discharge Pulse Power	W/kg	800	800
Discharge Pulse Power Density	W/l	1600	1200
Specific Regen Pulse Power	W/kg	430	400
Regen Pulse Power Density	W/l	860	600
Recharge Rate		C/3	C/3
Specific Energy	Wh/kg	200	400
Energy Density	Wh/l	400	600
Calendar Life	Year	10+	10
Cycle Life (at 30°C with C/3 charge and discharge rates)	Cycles	5,000	1,000
Operating Temperature Range	°C	-30 to +52	-30 to +65



Project Technical Targets

<u>**Year 1 (Gen 1):**</u>
Cell Level 230 Wh/kg, 1000 cycles (PHEV)

<u>**Year 2 (Final Deliverable Cells):**</u>
Cell Level 250 Wh/kg, 5000 cycles (PHEV), Cell Level 350 Wh/kg, 1000 cycles (EV)

First Year Technical Milestones

- Milestones leading to cell performance data from "Gen 1" cell build representing first try at integrating improved materials, electrolytes and cell designs.

Cell Build Progression:

Year 2

Baseline	→	*Gen 0*	→	*Gen 1*	→	*Gen 2*	→	*Final Deliverables*
LL-NCM/Graphite		*NCM/Graphite*		*Advanced Materials*		*Advanced Materials*		*Optimized System*

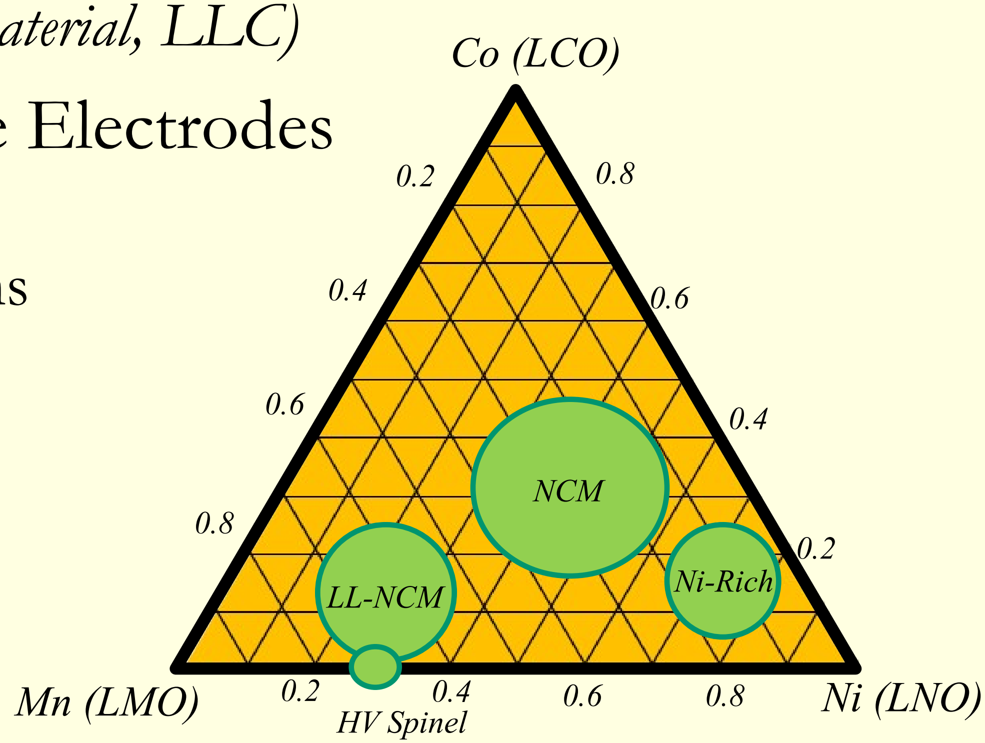
First Year Milestones and Status

Month	Milestone	Type	Description
Month 5	Completion of Baseline Cell Deliverables	Technical	High Voltage LL-NCM/Graphite pouch cells
Month 9	Completion of Round 1 Electrolyte Evaluation	Technical	Successful identification of candidate high voltage stable electrolyte formulations.
Month 11	Selection of GEN 1 Cathode Materials Complete	Technical	LLS-NCM, Ti-NCM, & Si Anode material selected using high voltage stable electrolytes
Month 12	Completion of GEN 1 Small Cell Build	Go/No Go	Energy density exceeding of 230 Wh/kg at a C/3 rate estimated from testing in a 200 mAh form factor with projected cycle life of > 1000 cycles

Technical Approach

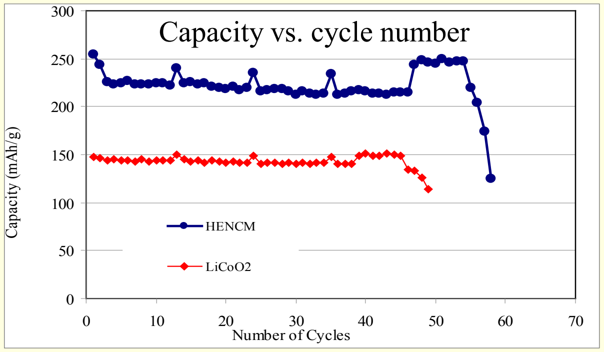
Development focused on addressing key current barriers to achieving high capacity long life Li-ion cells.

- Higher Capacity, Higher Voltage Active Materials
  - IE-LLS-NCM *(Argonne National Laboratory)*
  - Stabilized-NCM *(Lawrence Berkeley National Laboratory)*
  - Si-Graphite Composite *(OneD Material, LLC)*
- Higher Rate Capability Cathode Electrodes
  - Ion Exchange Synthesis
  - Composite Cathode Formulations
- Higher Voltage Operation
  - Cathode Surface Stabilization
  - Stable Electrolytes *(Dupont)*
  - Stable Separator *(Dupont)*

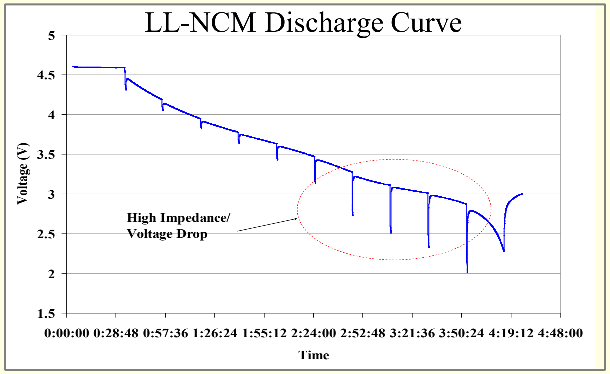


Technical Approach
Layered-Layered NCM

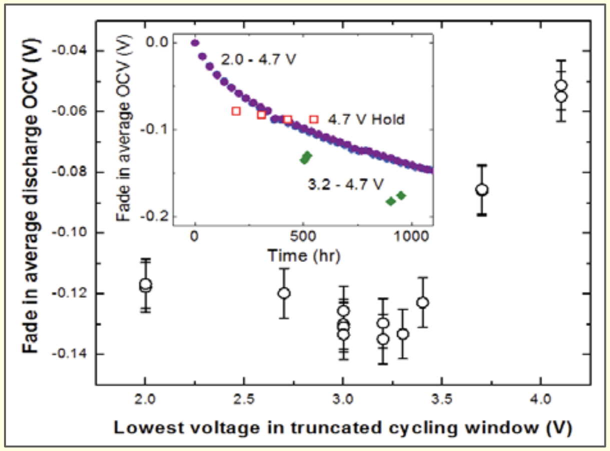
Advantages:
- High specific capacity – 230-250 mAh/g.
- Greater stability at high voltages.



Barriers:
- High impedance.
- State of charge dependent impedance and impedance growth.
- Voltage fade mechanism.
- Accelerated capacity loss if not stabilized.
- Low utilization in full cells.
- Low tap density.
- Wide voltage window.



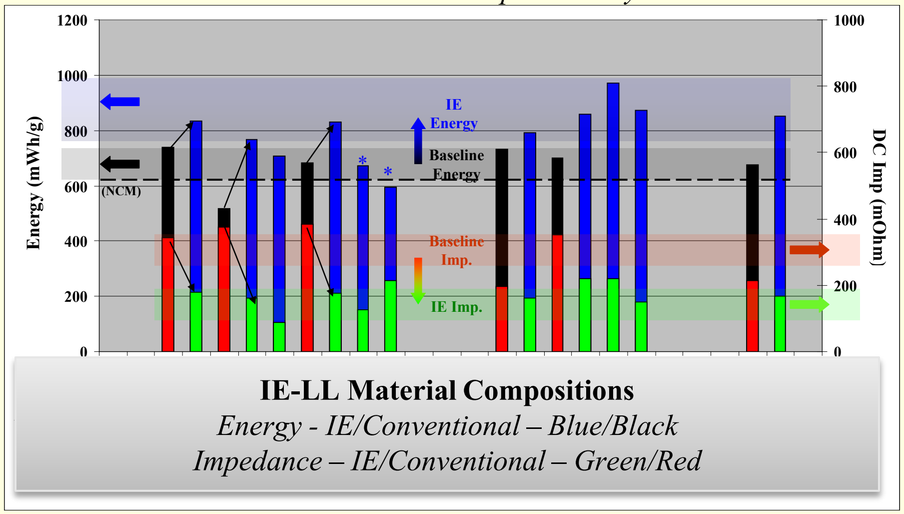
OCV drop during cycling LL-NCM within different voltage windows



Technical Approach
Layered-Layered NCM

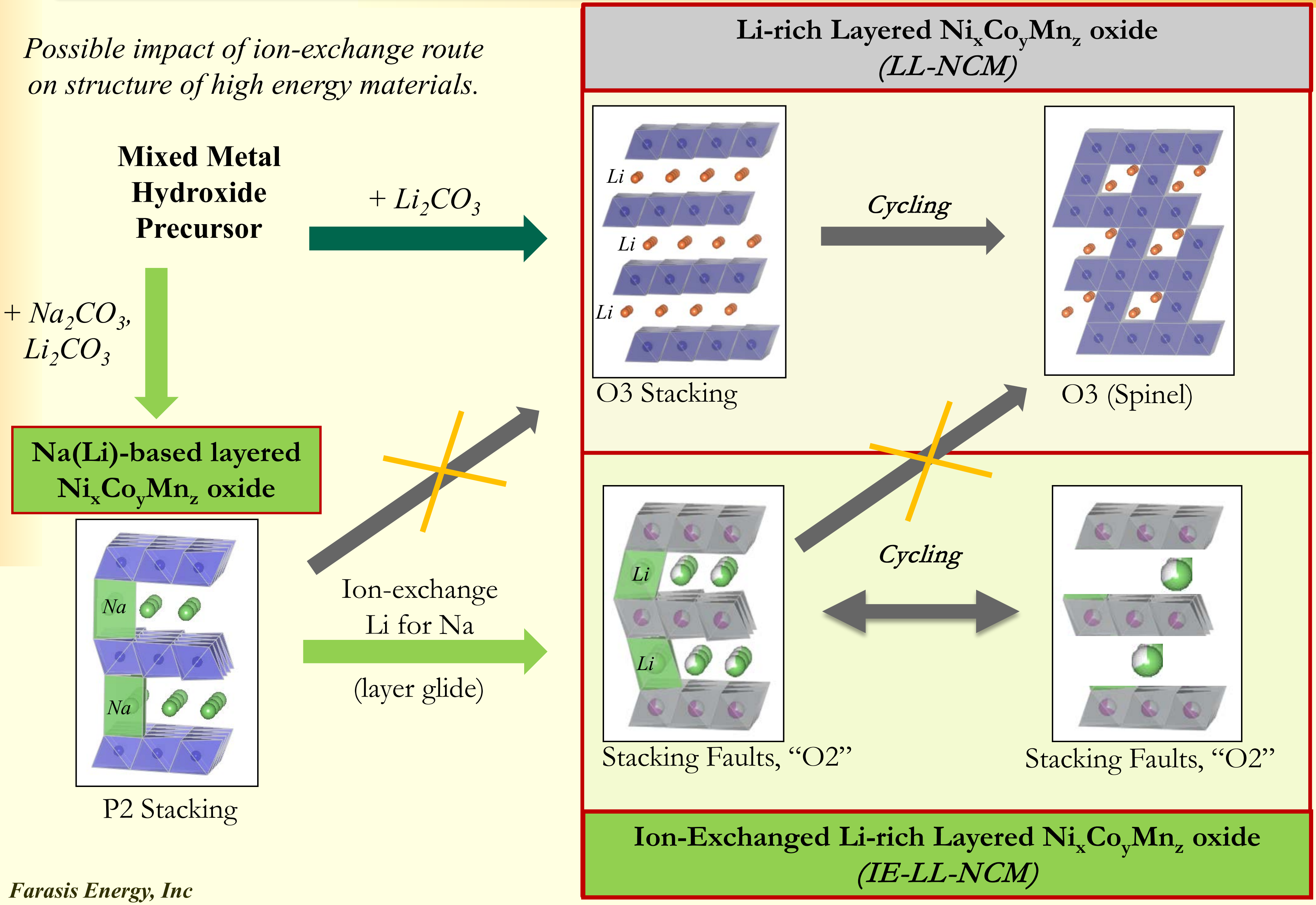
- Development strategy based on initial work done by Dr. Chris Johnson at Argonne National Laboratory and continued at Farasis Energy.
- Ion-Exchange Synthesis Approach
  - Na based LL-NCM material is used as a precursor to form Lithium LL-NCM through an ion-exchange process with Lithium (IE-LL-NCM)
  - Composition and synthetic conditions can be tuned to produce a high voltage spinel component to the LL materials → Layered-Layered-Spinel NCM (LLS-NCM)
  - Initial work indicates synthetic approach leads to materials with lower impedance and greater utilization.
- Potential for New Structural and Performance Characteristics
  - Potential to avoid O3 stacking and transition metal movement during cycling.
  - Route to creation of materials with larger interlayer spacings.
  - Route to introduce disorder into materials.
  - Route to materials with different surface morphology, stacking faults.

Comparison of energy and impedance measured for a number of IE and conventional LL-NCM compositions synthesized



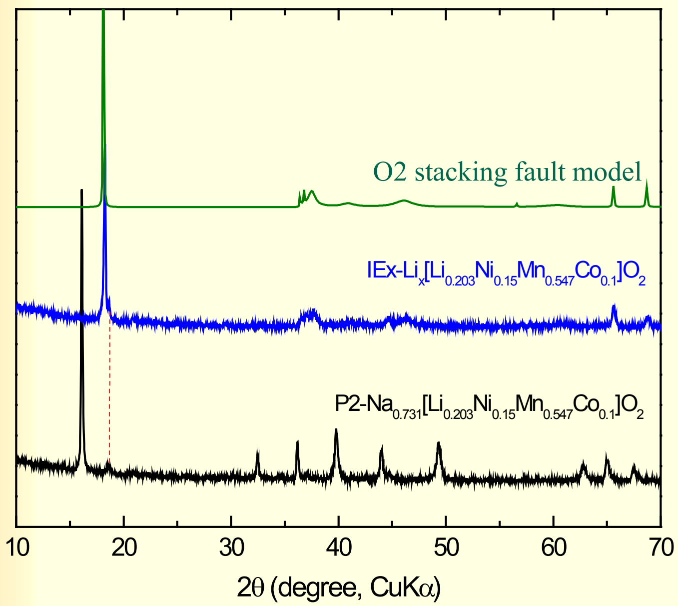
Ion-Exchange Synthesis of Layered-Layered NCM

Possible impact of ion-exchange route on structure of high energy materials.

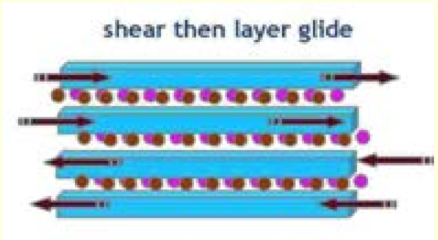


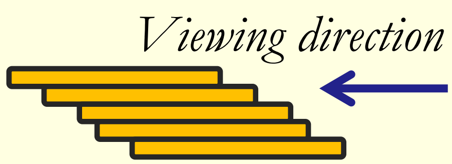
Ion-Exchange Synthesis of Layered-Layered NCM

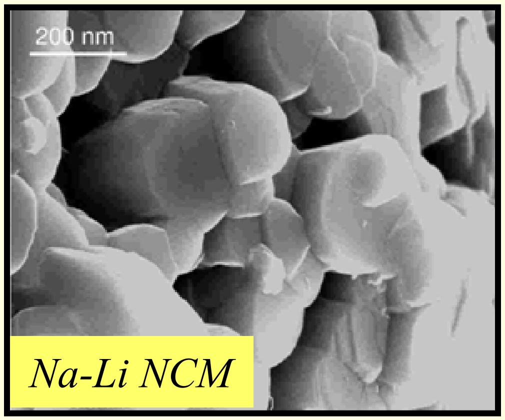
- X-ray diffraction indicates good layering order but significant disorder in other crystallographic directions suggesting presence of stacking faults.

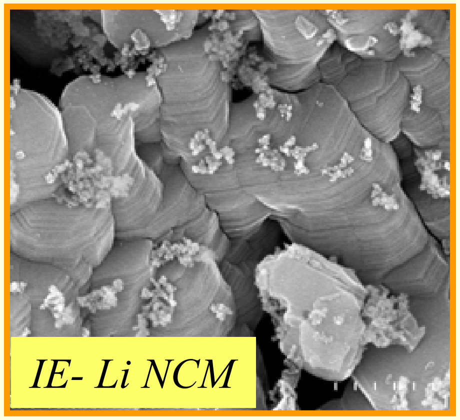


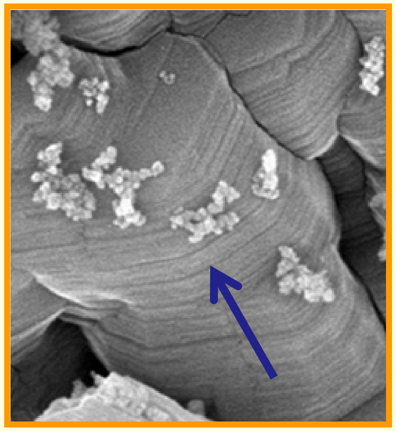
- Faults in shear order of crystal lattice during ion exchange
- Still strongly layered
- Local c-axis disorder
- Structural modeling indicates presence of extensive stacking faults with O2 layering characteristics.

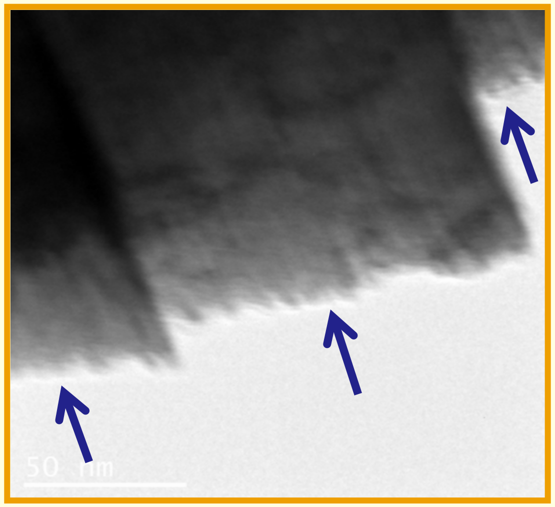










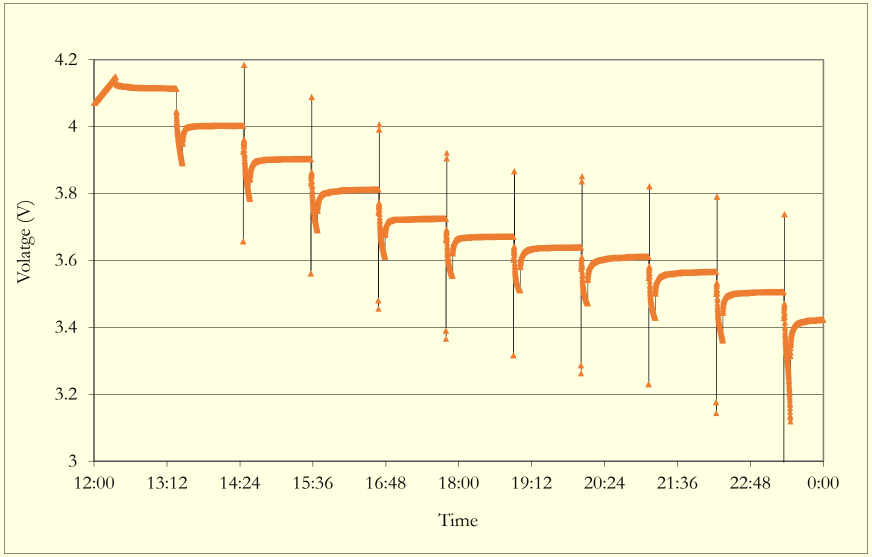


Technical Approach
Layered NCM Materials

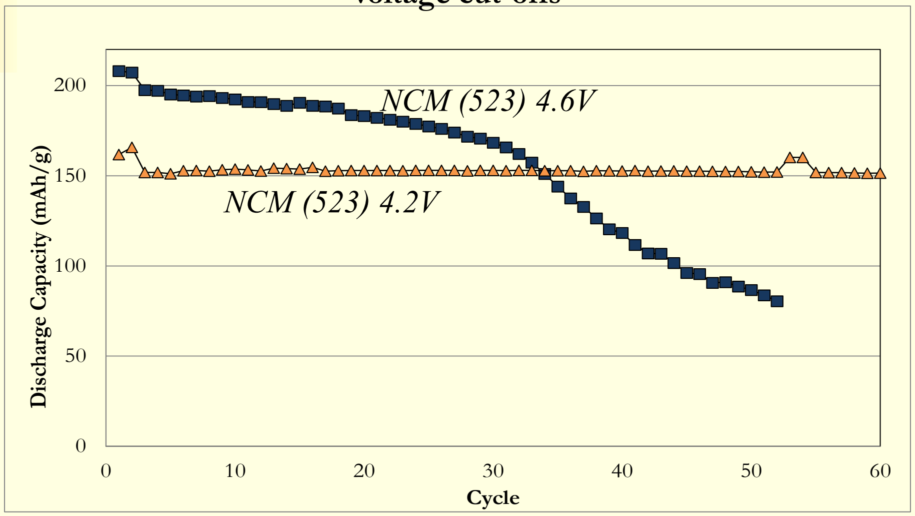
Advantages:
- Good rate capability
- High tap density
- Good stability at moderate voltages
- Reasonable average voltage

Barriers:
- Stability at high voltages.

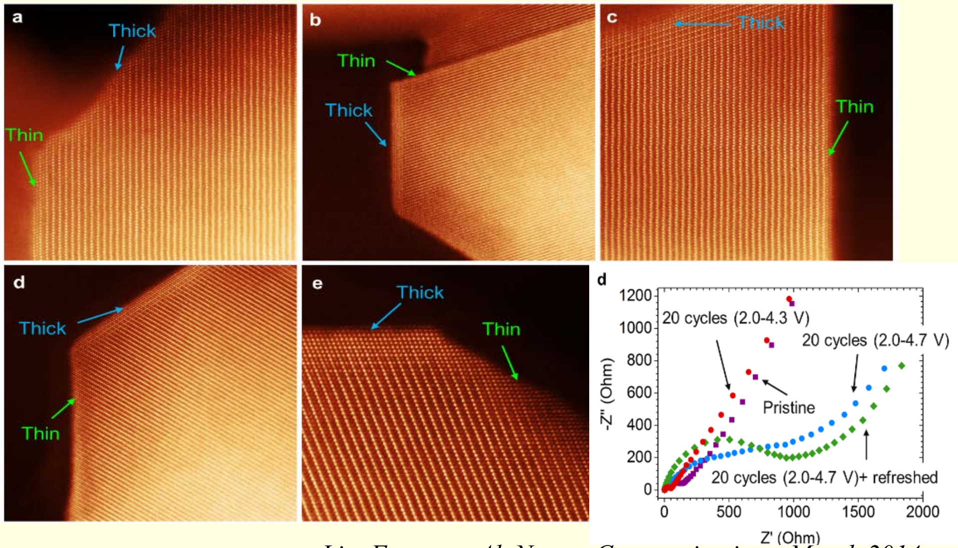
NCM/Graphite Cell HPPC test



Relative stability of NCM (523) cathode to different upper voltage cut-offs



Rock-salt surface reconstruction occurs upon electrolyte exposure alone, but is more severe when electrodes are cycled to 4.7V



Lin, Feng., et. Al, Nature Communications, March 2014

Technical Approach
Layered NCM Materials

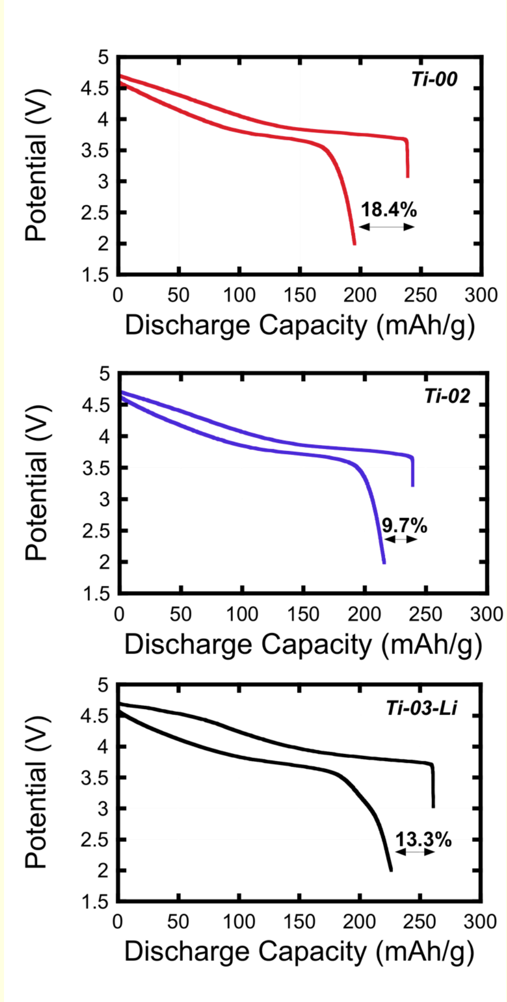
Surface Stabilization:

- Coatings/surface treatments.
- Decrease active material surface reactivity to electrolyte.

Doping:

- Bulk addition of elemental dopants to NCM composition.
- Stabilize layered structure in highly charged state.
- Aliovalent substitution to limit oxygen loss/surface reconstruction.

High Voltage Formation Curves of Ti-Doped NCM(424)

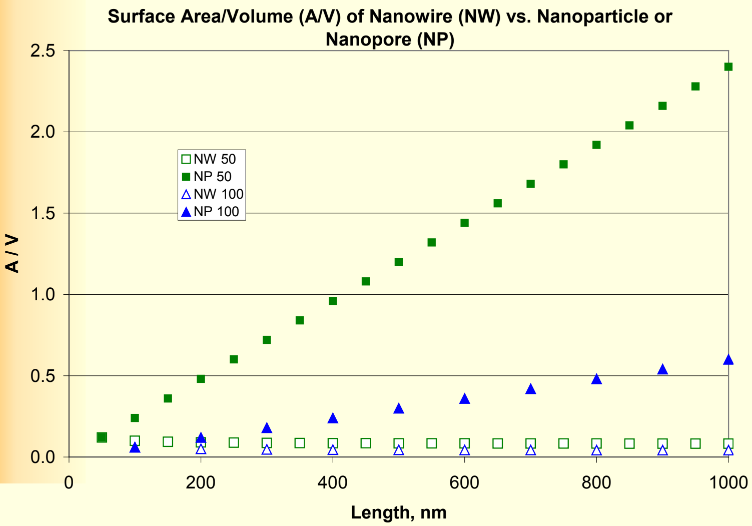


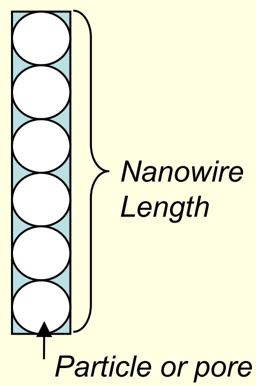
Kam, Kinson C., et. Al, J. Mater. Chem, 2011, 21 9991.

Technical Approach
Nano-Silicon Anode Materials

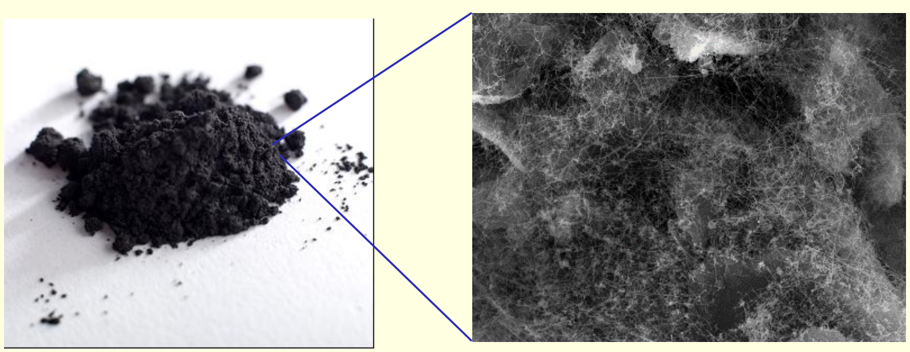
Nanosys SiNANOde Approach vs. Hollow/Porous Approach

SiNANOde	Hollow/Porous Si
Low A/V & Intact NW after cycling	High A/V; defects
Pack density similar to graphite	Pack density lower than graphite
Mass-produced with a competing cost * high Si utilization	Difficult and expensive to commercialize





- A Si nanowire is equivalent to several Si particles or pores with an identical diameter.
- Si nanowire has lower surface area/volume ratio (A/V) and hence less side-reaction with electrolyte and better cycle life



SiNANOde production process: Directly grow Si nanowires on graphite powders

- Cost effective and high Si utilization
- Improves dispersion in slurry and drop in process (just replace graphite powders)
- Si-C conductivity improvement
- Si% or anode specific capacity is controllable, focusing on **500 ~ 1600 mAh/g**
- High electrode loading, as high as 1.5g/cm^3
- Good cycling performance, cycled >1000 times

Technical Approach
High Voltage Li-ion Cell

- Develop high voltage capable fluorinated electrolytes with proper battery system design to enable operation up to 4.7 V:
    - Increase cell **Energy Density** by enabling higher voltages
    - Increase cell **Power Density** by maintaining/improving conductivity
    - Lower System **Costs** by enabling higher voltages, reducing number of cells needed and potentially simplifying packaging requirements
    - Good wettability will drive similar manufacturing processes
- Incorporation of separators that are inherently stable to high voltage operation.
- Improve adhesion stability of electrode laminates.
- Incorporation of low reactivity electrode laminate components.

Technical Accomplishments: Baseline Deliverable Cells

Milestone 1 (Month 5): Completion of Baseline Cell Deliverables

- LL-NCM/Graphite Li-ion Pouch Cells
- Capacity ~1.6 Ah
- Fourteen cells shipped to Idaho National Laboratory.
- Developing test plan with INL and DOE program managers.

Baseline Pouch Cell

Technical Accomplishments: High Voltage Electrolyte Development

Milestone 2 (Month 6): Completion of "Gen 0" Cell Builds

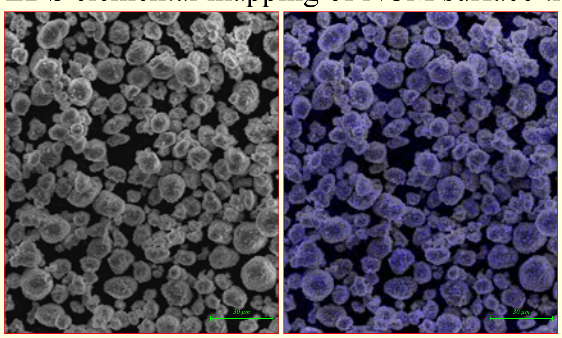
- "Gen 0" Cells for first round electrolyte development:
  - 18650 and pouch cells using conventional NCM/Graphite based chemistries designed for 4.4V and 4.6V operation.
  - Pouch cells using early stage advanced chemistries and silicon anodes.
- Ongoing work involves formulation optimization, formation protocols studies, failure mode analysis, gas generation measurements, accelerated testing.
- Have achieved significant gains in stability at high voltages relative to baseline carbonate electrolytes.

"Gen 0" Cells

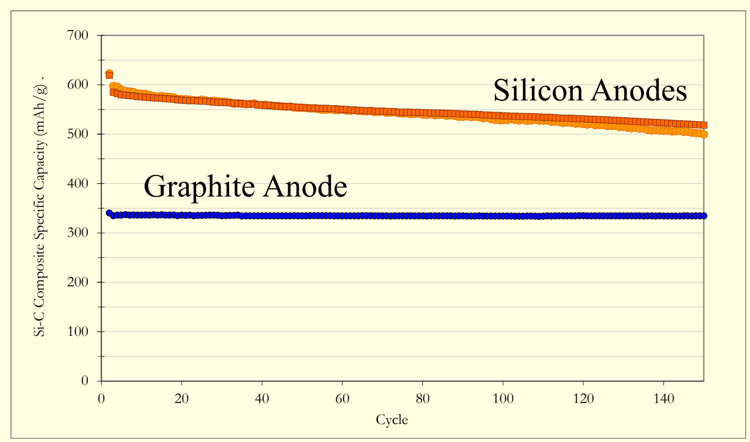
Technical Accomplishments Materials Development

- Received and characterized baseline materials from each subcontractor.
- Established uniform evaluation protocol for new cathode materials.
- Stabilized NCM –
  - Performed initial experiments to evaluate feasibility of low cost synthetic routes of doped NCM compositions.
  - Successfully scaled surface stabilization process for several NCM cathode compositions (0.5kg batches).
  - Cell design and initial evaluation of stabilized NCM materials at high voltage in full pouch cells.

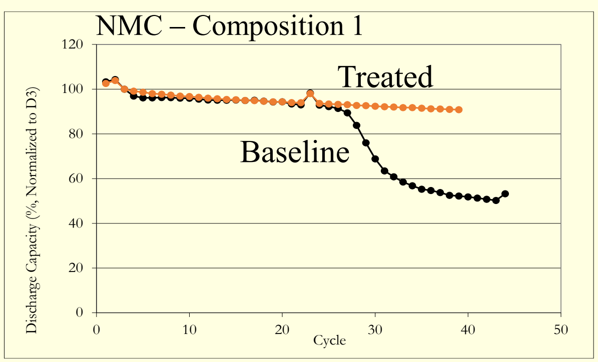
SEM/EDS elemental mapping of NCM surface treatment

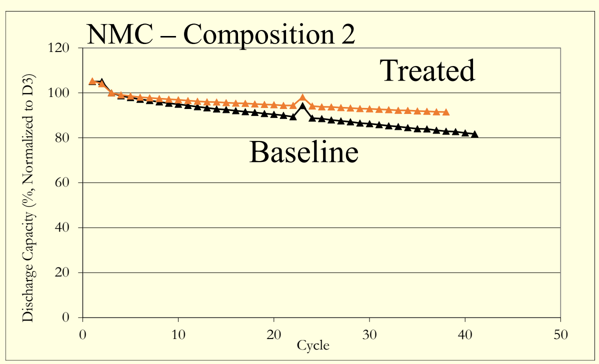


- Silicon Anode Development
  - Optimization of Si/Graphite electrode formulations.
  - Initial full cell evaluation against baseline cell cathodes.



Initial pouch cell evaluation of stabilized NCM materials at 4.6V

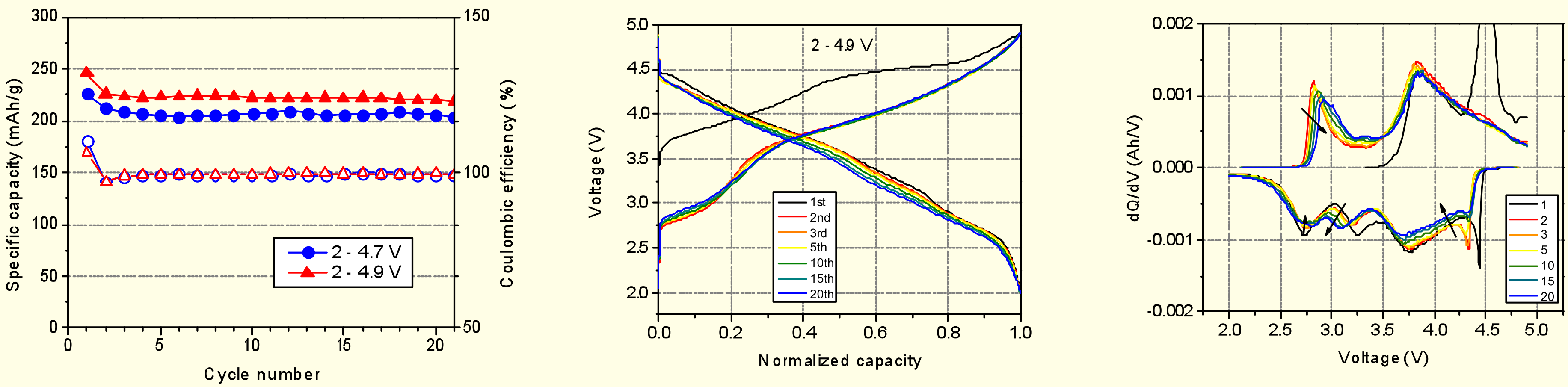




Technical Accomplishments
Materials Development

- Ion-exchanged LL-NCM
  - Started evaluation of compositional effects on material performance and structure.
  - Initiated experiments for comparison of lab scale ion-exchange materials against corresponding LL-NCM materials synthesized by conventional methods.
  - Initiated work on scaling ion-exchange processes.
  - Identified and are addressing issues associated with scaling ion-exchange processes.

$Li_x[Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.1}]O_{2-d}$ IE derived cathode material



Collaborations and Coordination with Other Institutions

Argonne National Laboratory (Chris Johnson)

Federal Laboratory – Subcontractor providing materials and analytical work for project.

- Layered-Layered-(Spinel) *(LL-S)* NCM Cathode Material Development – Developing an ion-exchange synthetic approach to address the impedance and voltage fade barriers of high capacity LL-NCM cathode materials.

Lawrence Berkeley National Laboratory (Marca Doeff):

Federal Laboratory – Subcontractor providing materials and analytical work for project.

- High Voltage Stabilized NCM Cathode Material Development – Develop and optimize doping and advanced coating methods to stabilize high capacity NCM materials to operation at high voltages.

Nanosys/OneD Material, LLC (Yimin Zhu):

Industry – Subcontractor providing materials and development guidance for project.

- Nano-Silicon Graphite Composite Anode Material Development – Optimize nano-silicon graphite composites for long term cycling stability.

Dupont (Srijanani Bhaskar):

Industry – Partner providing materials and analytical work for project.

- High Voltage Capable Electrolytes and Cell Components- Develop new fluorinated electrolyte systems, additives and separators with exceptional high voltage stability to advanced active materials.

Proposed Future Work

- Complete high voltage cell component development and evaluation in Gen 0 cells.
- Characterize failure mechanisms associated with high voltage cell operation in Gen 0 chemistry.
- Develop and optimize ion-exchange LL-NCM compositions for capacity, rate capability and stability.
- Perform detailed structural and electrochemical characterization of new materials and impact of compositional and synthesis variables on material.
- Evaluate new IE-LL-NCM materials using "voltage fade" protocols.
- Develop synthetic methods for making aliovalent doped NCM materials.
- Demonstrate improved stability and performance characteristics of stabilized NCM materials at elevated voltages.
- Select and scale synthesis of best materials for Gen 1 cell build.
- Further optimization of Silicon anode electrode for Gen 1 cell build.
- Plan Gen 1 cell build and design, build and test cells.

Summary Slide

- Project is relevant to the development of high energy Li-ion cells capable of meeting the PHEV40 and EV performance goals set out by DOE.
- Approach to addressing current cell level performance barriers based on strong advanced materials technical foundation.
  - Ion exchange synthetic approach to address impedance and voltage fade issues.
  - Doping and surface stabilization to improve high voltage stability.
  - Cell component development aimed at enabling long term high voltage operation.
- Strong coordination with subcontractors and partners with steps taken to allow parallel development of multiple cell components for incorporation into high performance cells.
- Future work will continue advanced cathode and anode material development and optimization leading to Gen 1 cell build at the end of Year 1.